ON THE MAGNETIC PROPERTIES OF METALS

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Abstract

It is shown that the susceptibility of copper and silver is structure sensitive. Annealing increases the diamagnetism and drawing decreases it. It is suggested that uncertainty concerning the state of a metal as well as uncertainty concerning its purity may account for the large spread of observed values of the susceptibility. It is shown that the Pauli paramagnetism of the free electrons and the diamagnetism of the ions taken together are not sufficient to explain the susceptibility of the alkali metals. It is suggested that partly bound electrons should be taken into consideration. Several effects are predicted by means of which the total susceptibility can be analyzed and its component parts measured separately.

OUR knowledge of the processes which contribute to the magnetic properties of metals has been considerably increased in recent years, but it has been impossible to submit any theories to an accurate experimental check because of the very large discrepancies between various observed values. The results for the susceptibilities of the alkali metals, for example, are contained in the following table.

Table I. *Specific susceptibility* $\times 10^6$.

	Honda[1]	Owen[2]	Bernini[3]	Sucksmith[4]	McLennan[5]	Lane[6]
Li	—	3.1 .5	3.8	—	—	—
Na	.51	.50	.54	.59	.59	.65
K	.40	.63 .58	.63	.51	.45	.54
Rb	—	.076	—	.07	.17	.21
Cs	—	−.10	—	−.05	.18	.22

The agreement is best for sodium, but even here the large value is 30% higher than the low one. Magnetic measurements on solids are so straightforward that it seems out of the question to attribute these discrepancies to experimental error, and it necessarily follows that different samples of these metals may have susceptibilities varying by amounts of the order of the susceptibility itself. In this connection, the question of impurities is an

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[1] K. Honda, Ann. d. Physik [4] **32,** 1027 (1910).

[2] M. Owen, Ann. d. Physik [4] **37,** 657 (1912).

[3] A. Bernini, N. cim. [5] **7,** 441 (1904); Phys. Zeits. **6,** 109 (1905). The value for Li is 3.8 and not 0.38 as given in the Landölt Bornstein tables.

[4] W. Sucksmith, Phil. Mag. [7] **2,** 21, (1926).

[5] J. C. McLennan, R. Ruedy and E. Cohen, Proc. Roy. Soc. [A] **116,** 468 (1927).

[6] C. T. Lane, Phil. Mag. [7] **8,** 354 (1929); Phys. Rev. [2] **35,** 977 (1930).

important one. It has generally been assumed that only ferromagnetic impurities could account for errors of such size, and in most of the work, iron has been tested for chemically and magnetically, and corrections applied on the assumption that the iron was present in its magnetically most active form. But even with such corrections, the agreement is poor, and it becomes necessary to find another reason for the disagreement between observed values.

A hint as to what this uncertainty in magnetic measurements on metals is due to is given by the following considerations. We now know that conduction electrons do play a part in magnetic phenomena; and we know that, in general, properties due to conduction electrons, such as conductivity, change of resistance in a magnetic field, etc., are structure sensitive properties. Consequently, it seems reasonable to suppose that magnetic phenomena are also structure senstitive. In other words, we suppose that the susceptibility of a metal can be altered by mechanical working. In order to test this assumption, I undertook a few simple experiments with the help of Mr. J. Foladare. We used the Gouy method.[7] The sample, in the form of a cylinder about 12 cm long and 1 or 2 mm in diameter, was suspended from one arm of a beam balance. The lower end of the sample was in a homogeneous magnetic field. The magnetic force in dynes is then given by

$$F = \tfrac{1}{2}KH^2A \tag{1}$$

where K is the volume susceptibility, H is the magnetic filed strength, and A is the cross-sectional area of the sample. Copper and silver wires were used. The copper was slightly paramagnetic, probably due to impurities, but the silver was diamagnetic and probably quite pure. The procedure for copper was to take a long piece of wire and to cut it into lengths of about 15 cm. These were then stretched by various amounts, and their susceptibilities measured. As the diameters were equal before stretching, the diameters after stretching are a measure of the total distortion. Typical results are given in Table II.

TABLE II. *The effect of stretching on the magnetic susceptibility of a copper wire.*

Susceptibility in arbitrary units	Diameter of sample after stretching
3.2	1.67 mm
3.4	1.63 mm
4.1	1.57 mm
4.8	1.41 mm

This shows that stretching increases the susceptibility. The last sample above was then annealed by heating to red heat for about 15 minutes in a quartz furnace. During the heat treatment the sample was immersed in a CO_2 atmosphere to prevent oxidation. After the sample had cooled off, it was again measured, and its susceptibility was found to have changed

[7] See for instance, E. C. Stoner, Magnetism and Atomic Structure, p. 40.

from 4.8 to 3.4. It was then stretched again, so that its diameter changed from 1.4 mm to 1.36 mm, and the susceptibility increased to 4.1. Silver gave similar results. For example, stretching a given sample so that its diameter changed from 1.66 mm to 1.56 mm changed its susceptibility from -4.2 to -3.3.

Although the data obtained are very few, until further information is available, it seems reasonable to suppose that, just as hardening in general increases the resistance of a metal, it also increases the paramagnetic component or decreases the diamagnetic component of its susceptibility. The significance of this result will be further discussed below. At this point, I merely wish to point out that structural features must be taken into account in subsequent measurements; that other mechanical deformations may play an equally important though different role (twisting, stretching within the elastic limit, compression, etc); and that impurities may have a considerable influence on the above effects, especially if the rate of cooling is taken into account.[8]

Let us return now to a closer examination of the experimental facts and their significance. For simplicity, I shall deal with the alkali metals, though many of the considerations apply to other substances as well. We have, then, experimental values for the susceptibility within a certain range for each substance, and it is proposed to determine something about the mechanisms which must be assumed to explain the results. Theoretically we know that there exist two components at least of the susceptibility. One is the diamagnetism of the ions in the metal. This, if measured per unit volume, is designated by K_i. It is independent of the temperature except when the number of free electrons is not constant, and its absolute value can be estimated both theoretically and experimentally. It is structure insensitive. The other component is the paramagnetism of the free electrons due to their spins, and has been calculated by Pauli.[9] It is also structure insensitive, and is given by one of the following formulae

$$K_p = \frac{1}{4\pi}\left(\frac{3}{\pi}\right)^{1/3}\frac{e^2}{mc^2}n^{1/3} \tag{2}$$

$$= \frac{1}{4\pi}\left(\frac{3}{\pi}\right)^{1/3}\frac{e^2}{mc^2}\alpha^2 n \tag{3}$$

$$= \frac{3}{10}\frac{n\mu^2}{\epsilon_0}. \tag{4}$$

Here it is assumed that there is one free electron per atom. n is the number of atoms per cm^3; α is the lattice constant, such that for a simple cubic lattice $\alpha^3 n = 1$; μ is the magnetic moment of the electron; and ϵ_0 is the zero-point energy of the electrons. The first form of the formula is most useful for com-

[8] W. G. Davies and E. S. Keeping, Phil. Mag. [7] **7**, 152 (1929).
[9] W. Pauli, Zeits. f. Physik **41**, 100 (1927).

parison with experiment, and will be discussed more fully below. The second form shows that K_p is comparable with K_i,

$$K_i = -\frac{1}{6}\frac{e^2}{mc^2}\Sigma r^2 n \tag{5}$$

where Σr^2 refers to the summation of the average value of r^2 over all the electrons in the ion. Thus for large ions with many electrons, it is to be expected that $|K_i| > |K_p|$, whereas for small ions like Li, as a more detailed consideration shows, $|K_i| < |K_p|$. The last form, Eq. (4), is perhaps most useful in anticipating what would happen in a metal in which some of the electrons are partly bound. Such a binding might be thought of as a dropping of electrons into potential energy holes, with a consequent decrease in ϵ_0 and an increase in K_p. In this sense formulae (2) and (3) may be thought of as lower limits which actual bodies approach when their electrons may be considered really free. Another way of interpreting the increase in susceptibility due to binding is to suppose that, as the electrons travel through the metal, they are occasionally caught by an atom, and add to the paramagnetism through their orbital motions. To these processes, one would still have to add any diamagnetism of the free electrons. A calculation of the quantity has been carried out[10] in an approximate fashion, and it has the same form as Eq. (3), but the numerical factor must be open to considerable doubt because in the approximation used any one cell in the lattice was assumed identical with all the others, thus omitting fluctuations which most certainly occur, and which may be of considerable importance for diamagnetism. The diamagnetism of partly bound electrons, especially those which are concerned in holding the atoms of the metal together, must also be considerable, especially in substances like bismuth with an unusually large diamagnetism which is known to be structure sensitive. In the case of bismuth and allied metals, it is certainly related to the unusual crystal structure, but it is well to keep in mind the possibility that in other metals a similar process may also take place, though of course to a much lesser extent.

The first point to be checked concerns the absolute values of the susceptibilities. Table III shows the situation.

TABLE III. *Comparison of theoretical and experimental values for the susceptibility of the alkali metals. Volume susceptibility* $\times 10^6$.

	K_p	K_i	K_p+K_i	K experimental
Li	.79	−.31	.48	.27 to 2.04
Na	.66	−.45	.21	.49 to .63
K	.51	−.37	.15	.35 to .55
Rb	.49	−.56	−.07	.14 to .34
Cs	.45	−.64	−.20	−.19 to .41

The values for K_i are taken from Stoner[11] and are dependable as to order

[10] F. Bitter, Proc. Nat. Acad. Sci. **16**, 95 (1930).

[11] E. C. Stoner, Magnetism, p. 101 (1930).

of magnitude except for Li, where the true value may be much nearer zero. The outstanding feature of the table is that the observed values are more paramagnetic than the calculated ones. Especially for lithium this seems to be the case. I measured a sample of Li in the form of a wire made by sucking molten Li into a glass tube, pulling the sample out by one end after it had cooled, and finishing the magnetic measurements rapidly in air before appreciable oxidation had set in. The result was a specific susceptibility equal to 3.8×10^{-6}, in good agreement with the larger values in Table I. A spectral analysis of the sample, for which I am indebted to Professor Badger, revealed chiefly magnesium and other alkali metals as impurities, with no detectable traces of iron, and in view of Owen's work, it does not seem possible that this high value is due to iron. A further investigation to determine the origin of the large discrepancy between 3.8 and 0.5 should prove very interesting. The possibility that a radio-active impurity might produce such a high value, perhaps through nuclear excitation, was also investigated, but this was found to be very improbable, as the zero count of a Geiger counter was not observably changed by the presence of the lithium in direct contact with the counter chamber.[12] Whatever these high values are due to, there unquestionably is another phenomenon to be considered, and this most probably is related to the partly bound electrons. More experimental data are needed to help in satisfactorily interpreting the spread of the observed values.

Besides measurements on pure substances, measurements on alloys of the alkali metals in each other should prove especially interesting, as these substances, except lithium, are not supposed to be crystalline at ordinary temperatures. If further investigation shows that accurately repeatable measurements can be made on pure substances, it would even be possible to check the dependence on n in Eq. (2) by determining whether the deviation from linearity of the susceptibility of these alloys as a function of concentration of the components was representable by the $n^{1/3}$ dependence on the density give in Eq. (2).

A further consequence of the assumption that a part, at least, of the susceptibility of metals is due to free electrons, is that there must exist a small "magneto-electric" effect, analogous to a thermo-electric effect. If one end of a wire is in a magnetic field H, the other end in a field zero, the electrons at the two ends have different energies, the difference being of the order of magnitude $\frac{1}{2}K_eH^2\text{ergs/cm}^{-3}$, where K_e is the volume susceptibility of the electron gas, and might be less than K_p above due to a possible diamagnetic effect.[13] If we assume $K_e=0.5\times10^{-6}$ and a very large $H=50{,}000$ gauss, such as might be used for such an experiment, this would give 625 ergs per cm^3. To calculate the energy per electron this quantity must be divided by n, which for silver, for instance, is 5.9×10^{22}, and we have about 1.1×10^{-20} ergs per electron. Translated into electron volts this gives 10^{-8}

[12] I am indebted to Dr. Van den Akker for performing this experiment for me.

[13] In this connection I want to point out that such a "magneto-electric" effect is to be expected for ferro-magnetic substances as well as others, though its order of magnitude cannot, so far as I am aware, be calculated.

volts as the potential difference for the two ends of the conductor. To detect such an effect would probably be difficult, but certainly possible. A convenient form would be that of the thermocouple, but instead of keeping the two junctions at different temperatures, it would be necessary to keep them at the same temperature, but at different field sterngths. In this way it would be possible to measure separately the susceptibility of the free electrons.

One more effect can be predicted; namely, a dependence of the susceptibility on the field strength in the neighborhood of Kapitza's critical field strength,[14] called by him H_k. These are the field strengths at which the dependence of the change in resistance on magnetic field goes over from a quadratic to a linear function. Above this field strength the susceptibility should approach a more paramagnetic value and should become more structure insensitive, and the difference in the susceptibility of an annealed wire above and below H_k should be of the order of magnitude of the change produced by annealing a hard drawn wire. These conclusions are based on the following picture of the mechanism. Kapitza's work has shown that some property of the electrons exists which has not been taken into consideration in the theoretical analyses. It is a property which controls the behavior of the electrons in a magnetic field, and is very probably related to the residual resistance and supra-conductivity. It is structure sensitive. Such a property is contained in the "large orbits" of bismuth electrons. For simplicity let us refer to it merely as an orderliness in the motion of some of the electrons in a lattice. This order is responsible to some extent for conduction and diamagnetism. Either a magnetic field or mechanical distortion has the effect of destroying this order, and consequently of increasing the resistance and decreasing the diamagnetism. The picture accounts in a rough way for the facts, and predicts the above mentioned dependence on the field strength above H_k. This "orderliness" must of course not be interpreted too literally. It is really only another way of referring to Kapitza's inner "fields."

[14] P. Kapitza, Proc. Roy. Soc. [A] **123,** 292 (1929).